The Spin-Echo Experiments and the Second Law of Thermodynamics

T.M. Ridderbos[1] M.L.G. Redhead[1]

Abstract

We introduce a simple model for so-called spin-echo experiments. We show that the model is a mixing system. On the basis of this model we study fine-grained entropy and coarse-grained entropy descriptions of these experiments. The coarse-grained description is shown to be unable to provide an explanation of the echo signals, as a result of the way in which it ignores dynamically generated correlations. This conclusion is extended to the general debate on the foundations of statistical mechanics. We emphasise the need for an appropriate mechanism to explain the gradual suppression over time of the correlations in a thermodynamic system. We argue that such a mechanism can only be provided by the interventionist approach, in which the interaction of the system with its environment is taken into account. Irreversible behaviour is then seen to arise not as a result of limited measurement accuracy, but as a result of the fact that thermodynamic systems are limited systems which interact with their environment. A detailed discussion is given of recent objections to the interventionist approach in the literature.

1 Fine-grained versus coarse-grained entropy

In this paper we will defend the objective interpretation of entropy as captured by the approach of counting on a logarithmic scale the number of accessible states of a system. Although we will base our discussion on the Gibbs entropy, we will argue against the method of coarse graining, introduced by Gibbs in order to obtain the Second Law of thermodynamics.

In the Gibbsean ensemble approach to statistical mechanics, the (fine-grained) entropy of a thermodynamic system consisting of n particles, each having f degrees of freedom, is defined by the functional

$$S_{fg} = -k \int \rho \ln \rho \, d\Gamma, \tag{1}$$

where ρ is the n-particle distribution function and the integral is over Γ-space, which is the $2fn$-dimensional space in which each point represents the complete dynamical state of one of the infinitely many systems in the ensemble. From this statistical mechanical analogue of the entropy one can derive the usual thermodynamical relations for systems in equilibrium. However, whereas the thermodynamic entropy increases for a system approaching thermodynamic equilibrium, in agreement with the Second Law of thermodynamics, the fine-grained entropy remains constant in time as a consequence of Liouville's theorem, which expresses the fact that the flow in phase space is incompressible:

$$\frac{d\rho}{dt} = 0. \tag{2}$$

[1]Department of History and Philosophy of Science, Free School Lane, Cambridge CB2 3RH, U.K.

The shape of the volume of the phase space occupied by the ensemble may change, but the volume itself remains constant. Therefore, there can be no approach to equilibrium from the fine-grained point of view.

To obtain the analogue of Boltzmann's H-theorem, which using the Stoßzahlansatz shows for the case of a dilute gas the existence of a unique equilibrium state that will be steadily and monotonically approached from any non-equilibrium state, Gibbs[(1)] introduced the method of coarse graining. The coarse graining method consists of dividing the phase space Γ into regions of small but finite volume, each region being still big enough to contain many phase space points. Some authors have argued that this method can be justified by the observation that the position of a system in the (classical) phase space Γ cannot be determined by experiment with unlimited accuracy. (In the quantum case one considers groups of eigenstates instead of individual eigenstates with the justification that the precise eigenstate of a system cannot be established by experiment.) According to this view, the volume of a region, or the number of eigenstates in a group, should correspond to 'the limits of accuracy actually available to us' (Tolman[(2)], p. 167). In the absence of a law of physics which determines the size of the boxes in which phase space has to be devided, the magnitude of the coarse-grained entropy change depends on the human choice of the size of the boxes, thus arguably introducing an element of subjectivity into statistical mechanics.

To derive the generalized H-theorem one defines a coarse-grained density

$$\bar{\rho}(\tau, P, t) = \frac{1}{\tau} \int_{\tau} \rho(P, t)\, d\Gamma, \tag{3}$$

where P are points in the phase space Γ, τ is the volume of the phase space regions into which phase space is divided and the integral is caried out over the volume element containing the point $P \in \Gamma$. The quantity $\bar{H}$ is then defined by

$$\bar{H} = \int \bar{\rho} \ln \bar{\rho}\, d\Gamma \tag{4}$$

Since $\bar{\rho}$ is not subject to the restriction expressed by Liouville's theorem, it follows that, unlike S_G, $\bar{H}$ need not remain constant in time.[2] We then have the following picture. When we start at $t = 0$ with an ensemble of systems whose phase space points are all located in the same box, at a later time the members of the ensemble will enter different boxes and become in general widely separated in phase space. Although the volume occupied by the ensemble will remain constant as a result of Liouville's theorem, it will change its shape in

[2]Consider a system at equilibrium at $t = t_0$. Suppose we are able to locate the particular box the system is in by a sufficiently precise measurement. All the members of the ensemble must then be located in that particular box at t_0. As a result of the principle of equal a priori probabilities ρ_0 is constant throughout this box and therefore $\bar{\rho}_0 = \rho_0$. We then change the macroscopic constraints of the system. One can prove that at a later time t_1 we have:

$$\bar{H}_0 \geq \bar{H}_1. \tag{5}$$

The proof is based on the fact that the function $f(x) = -x \log x$, $x > 0$, is strictly concave. However, it must be emphasized that although we can prove that $\bar{H}_0 \geq \bar{H}_1$ and similarly for another time $t_2 > t_1 > t_0$: $\bar{H}_0 \geq \bar{H}_2$, we can't prove $\bar{H}_1 \geq \bar{H}_2$. In other words, we can't prove that there will be a monotonic increase of entropy. We can only expect that there will be a high probability for the coarse-grained entropy to increase due to the continuous spreading of the ensemble over the available phase space.

such a way as to "cover" all of the available phase space, in the sense that coarse-grained uniformity of box occupation numbers will be obtained.

Several authors, such as P. and T. Ehrenfest[(3)], Farquhar[(4)], Landsberg[(5)] and Penrose[(6)], have claimed that the method of coarse graining is an indispensable technique for the understanding of non-equilibrium behaviour of thermodynamic systems. Farquhar[(4)] (p. 19) writes:

> It is specifically by way of coarse-graining that the reversible and irreversible aspects of the behaviour of a macroscopic system are reconciled – irreversibility is associated with that lack of detailed knowledge which may be obtained about the dynamical state of the system and which is expressed by coarse-graining, and it is only statistically defined quantities, such as are coarse-grained quantities, that do change irreversibly.

Penrose[(6)] (p. 211), in a similar vein, argues:

> To obtain a statistical entropy that cannot decrease, therefore, we must ... assume that it is only possible to observe the number of systems in each observational state, not the identities of the individual systems constituting this number.

The aim of this paper is twofold. First we will argue that the method of coarse graining has to be rejected as an entirely unsatisfactory approach to explaining the behaviour of non-equilibrium systems. This will be illustrated by a discussion of the spin-echo experiments. We will address the confusions which exists in the literature with regard to the implications of the spin-echo experiments. Second we will argue that the only satisfactory approach to non-equilibrium statistical mechanics is the approach called interventionism.[3] We will discuss the interventionist programme and we will show how it generates time-asymmetric results.

2 Time-reversal of the dynamical evolution

When Boltzmann proved his H-theorem, which showed that there exists a unique equilibrium state which will be steadily and monotonically approached from any non-equilibrium state, Loschmidt raised the following objection. Consider a gas whose microstate is exactly the same as the microstate of a gas that has reached equilibrium, except that the direction of motion of each molecule is reversed. Loschmidt argued that, since the microdynamical laws are time-reversal invariant, such a velocity-reversed system will trace a path through microstates that are each the velocity-reverse of those traced by the original gas in its approach to equilibrium. It then follows from Boltzmann's definition of the quantity H and the H-theorem that the velocity-reversed system moves

[3] In a number of recent papers[(7),(8)] on the problem of thermodynamic irreversibility it is argued that this problem was satisfactorily resolved by Maxwell, Thomson and Boltzmann more than a hundred years ago. However, we would like to express our disagreement with this view, since it is based on the use of the Boltzmann entropy. The increase of this entropy is achieved by embedding the actual microstate of a system in a class of possible microstates given the macroscopic constraints, an idea which is taken seriously only by the Gibbs ensemble approach.

monotonically and ceaselessly away from equilibrium. On the basis of this argument Loschmidt concluded that Boltzmann's H-theorem is incompatible with the laws of the underlying microdynamics.

In the early 1950's Erwin Hahn accomplished a velocity reversal for a real physical system in the so-called 'spin-echo' experiments. In the original experiments[(9),(10)] a sample of glycerin (whose molecules contain hydrogen atoms) is placed in a strong magnetic field B_z pointing in the z direction for a time sufficiently long to align the proton spins in that direction. Because of its magnetic dipole moment, a proton placed in a constant magnetic field precesses about the direction of the field.[4] The angular frequency of the precessional motion of a proton about the direction of a magnetic field B_z pointing in the z direction is given by

$$\begin{aligned} \omega_0 &= g_s\,\omega_L = g_s\,2\pi\,\nu_L \\ &= g_s\frac{\mu_N}{\hbar}B_z = \frac{\mu}{I_z\hbar}B_z, \end{aligned} \tag{7}$$

where $\nu_L = \frac{\nu_N}{\hbar}B_z$ is the so-called Larmor frequency, $\omega_L = 2\pi\,\nu_L$ is the Larmor angular frequency and $I_z\hbar$ is the intrinsic angular momentum of a proton. For a typical spin-echo experiment using protons in glycerine with a magnetic field $B_z = 0.7$ T throughout the sample, the resonant frequency ω_0 will be 29.8 MHz, which is in the radio-frequency (rf) region.

When the strong magnetic field pointing in the z direction has been applied for a time suffiently long to align all proton spins in the z direction, a small oscillating magnetic field $B_x \cos\omega t$ is applied, where ω is the average resonance frequency of the sample of nuclear moments. In other words, the rf pulse contains a circularly polarized component that rotates at the rate at which the protons' spin axes would precess, if they were out of alignment with the constant field and if it were the only field present. Therefore, from the vantage-point of the protons the pulse field seems constant in direction. Consequently the proton spins precess about both the pulse field and the constant field. The intensity of B_x may be adjusted in such a way that $\omega_1 t_\omega = \frac{\pi}{2}$, where ω_1 is the Larmor angular frequency with which the nuclear moments precess about the magnetic field in the x direction and t_ω is the duration of the rf pulse. The result is that the proton spins are tilted exactly 90 degrees by the rf pulse from the vertical (the direction of the constant field) into the xy-plane. Therefore, after the rf pulse has been applied the proton spins will precess in unison in the xy-plane.

Obviously the same result can in principle be obtained by first applying a strong field B_x pointing in the x direction, so that the proton spins are aligned along the x axis and then switching off the field B_x and applying a field in the z direction. The protons will then start precessing in unison about this field B_z.

[4] For quantum mechanical particles the magnetic dipole moment consists of two parts. As in the classical case there is a contribution from the orbital angular momentum. There is also a contribution from the intrinsic angular momentum (spin), which does not have a classical analogue. We then have the following expression for the magnetic moment μ of a proton:

$$\mu = (g_l l + g_s s)\frac{\mu_N}{\hbar}, \tag{6}$$

where l and s are the quantum numbers for the orbital angular momentum and the intrinsic angular momentum (spin) respectively, g_l and g_s are the gyromagnetic ratios for the orbital and intrinsic contributions to μ respectively and $\mu_N = \frac{e\hbar}{2m_p} = 5.05082 \times 10^{-24}$ J T^{-1} is the nuclear magneton. For a proton $g_l = 1$ and $g_s = 5.5856912 \pm 0.0000022$, as can be measured for "free protons" in which l does not contribute to μ.

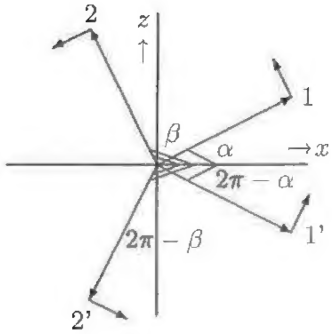

Figure 1: Reflection of the spin axes in the xy-plane as a result of the second rf pulse, demonstrated by two directions 1 and 2 inclined at angels α and β with respect to the x axis, reflected to orientations 1' and 2'.

The proton spins, precessing in unison about a common axis, resemble a giant spinning magnet. Like such a magnet, the protons emit an oscillating electromagnetic pulse; the free induction decay signal. This signal is the macroscopic evidence for the state of dynamic order the system is in by the end of the first rf pulse.

The dynamic order which has thus been created will decay in time, as a result of which the free induction decay signal fades away. The reason for this decay is the dependence of the precession frequency on the field-strength. Since the field B_z will not be completely homogeneous throughout the sample, the proton spins will precess with slightly different frequencies. Therefore, the spin axes will point in different directions after a time τ say. The sample is now in a state of apparent chaos.

At the time $t = \tau$ after the end of the first rf pulse we apply a second rf pulse. This pulse lasts twice as long as the first one, as a result of which the proton spins are tilted 180 degrees. Provided the spins remain in the xy-plane as a result of the smallness of the spin-spin interaction, the net result of the second rf pulse is a reflection of the spin axes in the xz-plane. This reflection reverses the ordering of the proton spins; the axes of the faster precessing spins which were pointing ahead of more slowly precessing spins will now be behind (see Fig. 1). Consequently, at a time τ after the end of the second rf pulse, the axes will be realigned, at which moment the atoms will emit another burst of radiation: the echo pulse. This echo pulse is the macroscopic evidence that the seemingly lost order has now been recovered.[5]

Once again, we can in principle obtain the same result without using rf fields. We would have to switch off the field in the z direction at a time τ after it was switched on. We then apply a constant field in the x direction. The proton spins will start precessing about the field in the x direction with a frequency ω'. This field must be switched off again after a time t' such that $\omega' t' = \pi$. In other words, the field in the x direction must be applied for a time long enough to make the protons complete half a revolution in their precession around the x axis. When the reflection of the spin axes in the xz-plane has thus been completed, resulting in a reversed ordering of the spin axes, the field in the x

[5]Later experiments have demonstrated the production of the echo signal in the presence of interaction between the spins. See for example[(11)].

direction is switched off and instead the field in the z direction is once again applied, causing the proton spins to precess about the z axis. The spins will then be aligned along the x axis at a time τ after the field in the z direction was switched on for the second time, resulting in an echo signal.

The reason the experiments are done using rf fields is that this type of experiment is used to measure magnetic moments and gyromagnetic ratios accurately, using resonance phenomena. In order to be able to obtain an echo signal using constant fields one would need to know the values of the magnetic moments and the gyromagnetic ratios from the start.

Hahn[12] has given us an analogy which clarifies the underlying mechanism of the spin-echo experiments. The spin-echo experiments can be likened to the case of a group of runners at a circular race track. At the beginning of the race all the runners are in line; a highly ordered state. When the starter fires his gun at time $t = 0$ all athletes start running with different velocities. After a while the runners are spread out over the race track. For someone who didn't see the start of the race it looks as if there is no particular relationship between the positions of the various runners on the race track. However, if the runners turn around and start running in the opposite direction upon a second firing of the starter's gun at time τ, the fastest runners are now in the rear and the slowest runners are ahead of the others. (One has to take into account that the runners might have started to overtake each other of course.) After a time 2τ the original situation will have been restored; all runners will pass the starting line at the same moment. This situation might be called a Loschmidt-reversal.

If we now turn to the spin-echo experiments we see that here we don't have a Loschmidt-reversal in the true sense of the word; the precessional motion of the proton spins about the field in the z direction is not reversed. However, we saw that the second rf pulse causes the spin axes to be reflected in the xz-plane, as a result of which the ordering of the directions in which the spin axes are pointing is reversed. This reversal of the ordering is equivalent to a reversal of the precessional velocities in the sense that the effect of the reversal of the ordering is the same as the effect of a velocity-reversal: the slower precessing spins are now ahead of the faster precessing spins. In time the faster precessing spins will catch up with the slower precessing spins, resulting in a return to the initial situation at $t = 2\tau$.

One could of course use a different experimental set-up in which the direction of the precessional velocities of the spins would actually be reversed, instead of using an rf pulse to reflect the spin axes in the xz-plane. Such a velocity-reversal could be achieved by reversing the direction of the field B_z. The difficulty here would be to reverse the direction of the field in a way which doesn't affect the angles between the axes of the different nuclear spins.

3 A simple model

We will now turn to a more detailed study of the time evolution of the system of nuclear spins in a spin-echo experiment. Using a simplified model we will be able to draw conclusions about the essential features of the behaviour of a nuclear spin system in a spin-echo experiment.

Our model consists of a continuous system, in contradistinction with the discrete systems we are dealing with in the case of a nuclear spin system or the

runners on a racetrack. The reason for introducing a continuous system is that we want to avoid recurrence phenomena, which is an essential complication of the discrete case.

The important feature our model has in common with both the nuclear spin system and the runners on the racetrack is that of a periodic motion. Let us consider an abstract thermodynamic system which is defined as a phase space X, a σ-algebra $\mathfrak{A}$ of subspaces of X and a measure μ defined on this σ-algebra $\mathfrak{A}$. The phase space we will be concerned with is the 2-dimensional phase space $X = \{(x, \omega) \mid 0 \leq x < 2\pi,\, 0 \leq \omega \leq \omega_m\}$. On this phase space the temporal evolution of the system is described by a dynamical law $S_t : X \to X$, $t \geq 0$, which is given by $S_t(x, \omega) = (x + \omega t - n \cdot 2\pi,\, \omega)$, where $n = \text{int}\left(\frac{x+\omega t}{2\pi}\right)$ (the map int: $\mathbb{R} \to \mathbb{N}$ maps any $x \in \mathbb{R}$ to the greatest possible $n \in \mathbb{N}$ such that $n \leq x$).

Let us assume that at time $t = 0$ we have a uniform distribution on a small part of the phase space $(x, \omega) \in \{(x, \omega) \mid 0 \leq x \leq \delta,\ 0 \leq \omega \leq \omega_m\}$, where $\delta \ll 2\pi$ rad. In other words, at $t = 0$ the density $\rho_0 \equiv \rho(t = 0)$ is given by:

$$\begin{aligned} \rho_0 &= \tfrac{1}{\omega_m \delta}, \quad 0 \leq x \leq \delta \\ &= 0, \qquad \delta < x < 2\pi, \end{aligned} \tag{8}$$

so that

$$\int \rho_0 dX = \int_0^{2\pi} \int_0^{\omega_m} \rho_0 d\omega dx = 1. \tag{9}$$

Under the time evolution defined by the dynamical law S_t the density $\rho(t)$ takes a different form. The effect of the dynamical law on the distribution $\rho(t)$ is illustrated in Fig. 2. Effectively, the initial vertical 'strip' of non-vanishing density becomes an oblique strip of equal area and slope $\frac{1}{t}$, which is stepped back a horizontal distance 2π, wherever it crosses the $x = 2\pi$ line, thus producing the series of parallel equally spaced striations shown in the figure. The exact analytical expression for $\rho(t)$ is given in Appendix A.

We now introduce a coarse graining of the phase space $X = \{(x, \omega) \mid 0 \leq x < 2\pi,\, 0 \leq \omega \leq \omega_m\}$. (Notice that this is a coarse graining of the individual so-called μ-space rather than the total so-called Γ-space). Let us assume that the size of the boxes of the coarse graining is $\Delta x \Delta \omega$, with $\Delta x \ll 2\pi$, $\Delta\omega \ll \omega_m$ (see Fig. 3). We define a coarse-grained distribution $\bar{\rho}(k, t)$, which is constant in each individual box k, by

$$\bar{\rho}(k, t) = \int_{x_k}^{x_k + \Delta x} \int_{\omega_k}^{\omega_k + \Delta\omega} \rho(t)\, d\omega dx. \tag{10}$$

In other words, the coarse-grained distribution is defined by dividing the portion of the original distribution which is in box k at time t by the area of the box $\Delta x \Delta \omega$. What the method of coarse graining can be seen to be doing here is to effectively ignore the fact that the shape of the area of the 2-dimensional phase space occupied by the distribution is very complex; it has a highly striated structure. The coarse-grained density doesn't recognize this structure, instead it introduces a distribution in each individual box which is uniform over the whole of the box.

When we compare the time evolution of the fine-grained and the coarse-grained distributions we find the following. It is very easy to see in an intuitive

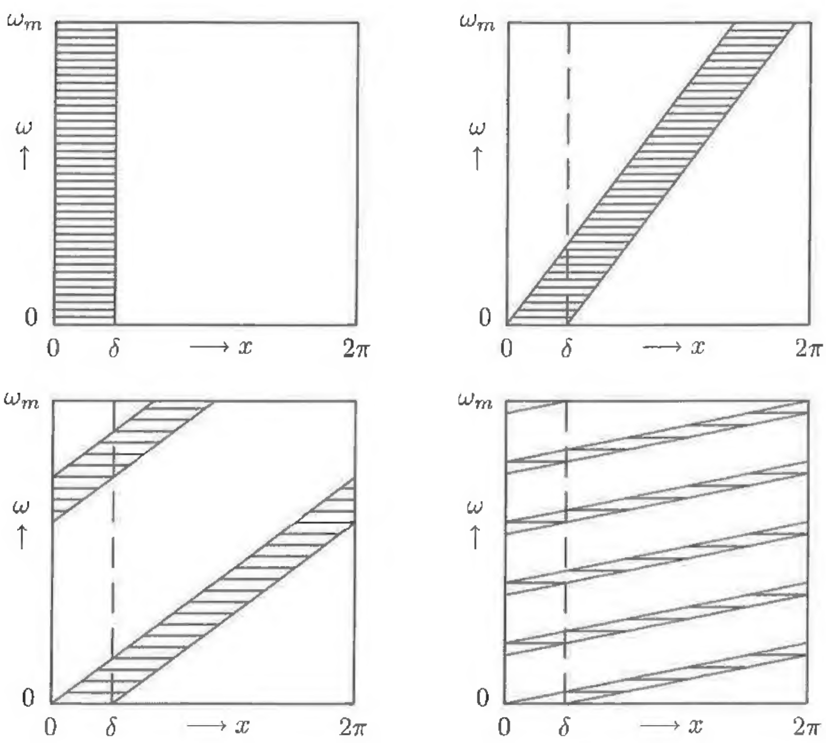

Figure 2: The effect of the dynamical law S_t on the density distribution $\rho(t)$, for $t = 0$ and subsequent values of t.

way that for $t \to \infty$ the coarse-grained distribution will approach a uniform distribution, as we expect. (See Appendix B for an exact derivation of this result.) The separation of the striations along the ω-axis is equal to $\frac{2\pi-\delta}{t}$. For $\delta \to 2\pi$ the separation vanishes and the distribution remains at all times uniform over the phase space $X = \{(x, \omega) \mid 0 \le x < 2\pi, 0 \le \omega \le \omega_m\}$. For $\delta \ll 2\pi$, the separation $\simeq \frac{2\pi}{t}$, which for $t \to \infty$ approaches zero. Similarly, the width of the striations in the ω-direction is equal to $\frac{\delta}{t}$, approaching zero for $t \to \infty$. On the other hand, the ratio $\frac{\textbf{width}}{\textbf{separation}} \simeq \frac{\delta}{2\pi}$ is independent of t. Furthermore, as we stated before, the slope of the striations is equal to $\frac{1}{t}$, which goes to zero for

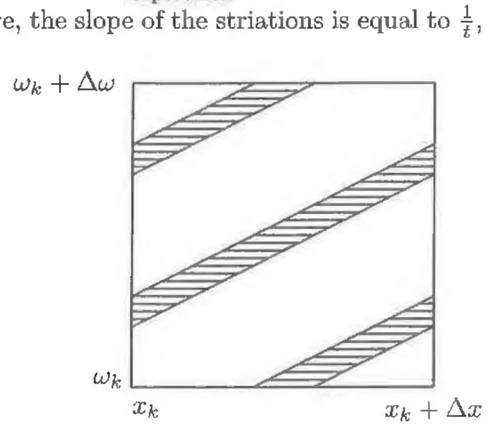

Figure 3: Coarse graining of the phase space X, illustrating the k^{th} box.

$t \to \infty$. So for sufficiently large t the striations become effectively horizontal, of vanishing width and separation. The area occupied by striations in any part of the phase space X of area A approaches $\frac{\delta}{2\pi} \cdot A$. (Note that this result is true even when $\delta \not\ll 2\pi$.) Applying this to a coarse graining box of size $\Delta x \Delta\omega$ we find that in the limit for $t \to \infty$ the fine-grained probability $\frac{\delta}{2\pi} \cdot \frac{1}{\delta\omega_m} \cdot \Delta x \Delta\omega$ is spread out uniformly over $\Delta x \Delta\omega$ producing a coarse grained density $\bar{\rho} = \frac{1}{2\pi\omega_m}$ which is uniform over the phase space X.

We can now compare the final coarse-grained entropy S^f_{cg} to the fine-grained entropy S_{fg}, using equation (1). (The initial coarse-grained entropy S^i_{cg} is of course equal to the fine-grained entropy S_{fg}, the distribution at $t = 0$ being uniform over $X = \{(x, \omega) \mid 0 \leq x \leq \delta,\, 0 \leq \omega \leq \omega_m\}$.) We find:

$$\begin{aligned} S_{fg} &= -k \int \rho \ln \rho \, dX = k \ln(\delta\omega_m) \\ S^f_{cg} &= -k \int \bar{\rho} \ln \bar{\rho} \, dX = k \ln(2\pi\omega_m). \end{aligned} \tag{11}$$

In other words, whereas the fine-grained entropy remains constant, the coarse-grained entropy increases by $\Delta S_{cg} = k \ln\left(\frac{2\pi}{\delta}\right)$.[6]

Two remarks may be made here. The first remark concerns the reason why in this case coarse graining leads to a uniform coarse-grained distribution. If the dynamical law describing the time evolution of the system would have simply been given by $S_t(x,\, \omega) = (x + \omega t,\, \omega)$ with $(x,\, \omega)$ a point in the two-dimensional phase space $X = \{(x, \omega) \mid 0 \leq x,\, 0 \leq \omega \leq \omega_m\}$ no striations would develop (or rather, we would have one long striation) and the system would never reach a state where each box of the coarse graining would contain an equal portion of the original distribution. It is the periodicity of the dynamical law S_t which opens up the possibility of a uniform coarse-grained distribution.[7]

The second remark concerns the fact that the uniform coarse-grained distribution is only achieved in the limit for $t \to \infty$. The dynamics of the system satisfies the mixing condition (i.e. in the limit as time goes to infinity the proportion of a coarse graining box occupied by points which at $t = 0$ were in the region $X = \{(x, \omega) \mid 0 \leq x \leq \delta,\, 0 \leq \omega \leq \omega_m\}$ approaches the relative proportion of the available phase space occupied by the original distribution), but

[6] In the case of the spin-echo experiments, where we have N independent particles, the final entropy of the system as a whole is given by

$$\begin{aligned} S^{tot}_{fg} &= -k \int \rho_{tot} \ln \rho_{tot} d\Gamma \\ &= -k \int \rho^{(1)} \ln \rho^{(1)} dX^{(1)} \cdot \int \rho^{(2)} \ln \rho^{(2)} dX^{(2)} \cdots \int \rho^{(N)} \ln \rho^{(N)} dX^{(N)} \\ &= Nk \ln(\delta\omega_m) \\ S^{tot}_{cg} &= Nk \ln(2\pi\omega_m) \end{aligned} \tag{12}$$

The increase of the coarse-grained entropy for the system as a whole is therefore equal to $\Delta S^{tot}_{cg} = Nk \ln\left(\frac{2\pi}{\delta}\right) = nR \ln\left(\frac{2\pi}{\delta}\right)$, with $n = N/(\text{Avogadro's number})$.

[7] Note that a similar situation exists in the case of a gas expanding from an initial volume V_1 into a final volume V_2. (This example is discussed in some detail by Denbigh and Denbigh[13] (pp. 57-61).) The finite spatial dimensions of μ-space generate boundary conditions: the reflection of the gas molecules at the walls of the container fulfills the same role as the periodicity of the dynamical law in our model, enabling the system to reach a coarse-grained equilibrium state.

is doesn't satisfy a stronger randomization condition, that is, the system is not a K-system or a Bernoulli system.

This can be illustrated by a computation of the behaviour under the time evolution of the quantity

$$M(t) = \int_0^{2\pi} f(x,t) \cos x dx, \tag{13}$$

where $f(x,t)$ is the density function representing the marginal distribution in x at time t. In our model the quantity $M(t)$ is the analogue of the averaged magnetic moment of the spin system in the x-direction, i.e. the initial direction of magnetization. The computation of the value of $M(t)$ is given in Appendix C. As is shown there, $M(t)$ is proportional to $\frac{\sin(\omega_m t)}{t}$. This means that the system exhibits decaying fluctuations in the magnetic moment (which might be called "bounces", rather than the echo which is induced by the second rf pulse). The magnitude of the fluctuating magnetic moment only vanishes in the limit as $t \to \infty$. Thus we see that even for macroscopic quantities equilibrium is not being achieved at finite times.

We do not claim, of course, that it is a virtue of our model that it is a mixing system and has no stronger ergodic properties. On the contrary, our remarks about the infinite times the system needs to reach the equilibrium state points to the problematic aspects of approaches based on mixing properties, since we are convinced that statistical mechanics should reproduce the finite relaxation times we find in real thermodynamic systems. The interventionist approach we defend later in this paper makes no reference to ergodic theorems, and may be expected to produce more realistic relaxation times to true equilibrium even for mixing systems. ~~(In general we reject ergodic approaches since they do not appear to be relevant for realistic systems.)~~

We will now study the behaviour of the model system under a reversal of the direction of the dynamical evolution, analogous to the case of the runners on the racetrack. We assume that the dynamical evolution is reversed at $t = \tau$, that is, for $t > \tau$ we have $t \to -t$, The dynamical law takes the following form for $t > \tau$: $S_t(x, \omega) = (\omega(2\tau - t) - n \cdot 2\pi,\, \omega)$, where $n = \text{int}\left(\frac{\omega(2\tau - t) + x(t=0)}{2\pi}\right)$. The effect of reversing the direction of the dynamical evolution at $t = \tau$ on the (fine-grained) probability distribution is that the evolution of the distribution in time for $\tau \leq t \leq 2\tau$ is the time-reverse of the evolution of the distribution under the dynamical law for $0 \leq t \leq \tau$. In other words, for all $\tau \leq t \leq 2\tau$ we have $\rho(x, \omega,\, t) = \rho(x, \omega,\, \tau - (t - \tau))$. For $t = 2\tau$ the system will have returned to its initial state, i.e. at $t = 2\tau$ we will have a uniform distribution over the region of the phase space $(x, \omega) \in \{(x, \omega) \mid 0 \leq x \leq \delta, 0 \leq \omega \leq \omega_m\}$. It is this return to the initial state upon the time-reversal of the dynamical evolution which explains the echo signal in the spin-echo experiments.

As was pointed out in section 2, it is important to realize that in the case of the spin-echo experiments it is not the direction of the dynamical evolution which is reversed, i.e. here it is not the case that t is replaced by $-t$ for $t \geq \tau$. Indeed, the system evolves under the same dynamical law S_t for $0 \leq t \leq \tau$ as for $\tau < t \leq 2\pi$. Instead, at $t = \tau$ the system undergoes a reflection in the xz-plane, that is at $t = \tau$ we have $x \to (2\pi - x)$. Therefore, instead of $\rho(x, \omega,\, t) \to \rho(x, \omega,\, \tau - (t - \tau))$, we now have for $t > \tau$ that $\rho(2\pi - x, \omega,\, t) = \rho(x, \omega, 2\tau - t)$. As a result we have at $t = 2\tau$ a uniform distribution over the region of the phase

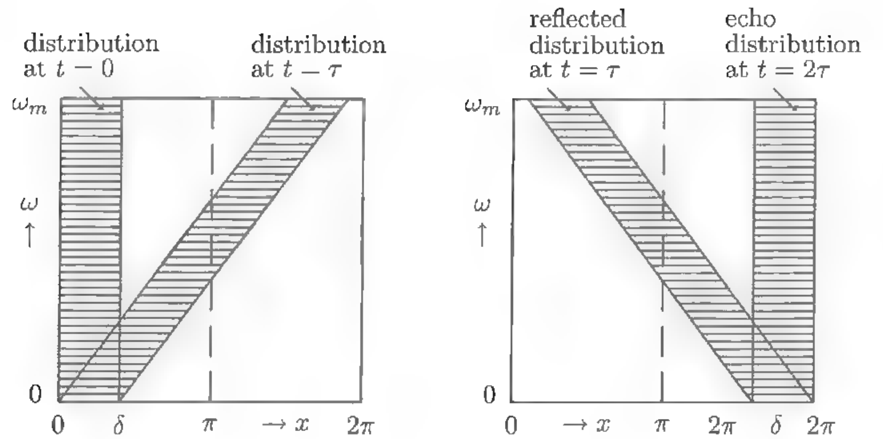

Figure 4: Behaviour of the distribution under the transformation $x \rightarrow (2\pi - x)$.

space $(x, \omega) \in \{(x, \omega) \mid 2\pi - \delta \leq x < 2\pi,\ 0 \leq \omega \leq \omega_m\}$, which is the reflection in the xz-plane of the part of the phase space over which we had a uniform distribution at $t = 0$ (see Fig. 4).[8]

Returning to our model system, we see that the effect of the map $t \rightarrow -t$ on the coarse-grained probability distribution differs in crucial aspects from the effect of this map on the fine-grained distribution. A reversal of the dynamical evolution in the coarse-grained case does not cause the distribution to evolve back to its original form. Starting from a uniform (coarse-grained) distribution over the entire phase space $X = \{(x, \omega) \mid 0 \leq x < 2\pi,\ 0 \leq \omega < \omega_m\}$ at $t = \tau$, the system will evolve under the dynamical law to the same uniform distribution for all $t > \tau$. That is, once the system has reached the equilibrium state, the system will remain in equilibrium. Similarly, when a time-reversal is applied to a coarse-grained distribution which has not yet reached the uniform equilibrium distribution, the system will continue to progress steadily towards a uniform coarse-grained distribution, rather than returning to its initial state.

4 Correlations

From the foregoing discussion it is obvious that the practice of coarse graining leads to a situation in which we are unable to account for the echo signals in the spin-echo experiments, the reason being that ignoring the striated structure of the probability distribution amounts to ignoring the correlational information stored in the system, as was first pointed out by Blatt[(14)]. From a coarse-grained perspective, where the emphasis is on the dissipation of macroscopic order into macroscopic disorder, it appears that the nuclear spin system is in a state close to equilibrium at $t = \tau$ after the first rf pulse has been applied:

[8]In practice, we won't have a uniform distribution of angular frequencies over the interval $0 \leq \omega \leq \omega_m$. Rather we will have a distribution over a small range of angular frequencies $\omega_0 - \Delta < \omega < \omega_0 + \Delta$, where ω_0 is the average resonant angular frequency in the sample and the value of Δ as well as the actual form of the distribution over the range of frequencies depends on the field gradient. We may assume a constant field gradient $G = \left(\frac{\partial B_z}{\partial l}\right)_{av}$ to exist throughout the sample, where l is any direction in which the field gradient has the given average value. Typical values for G in a spin echo experiment vary from $G = 0.2 \cdot 10^{-4}$ T cm^{-1} to $G = 0.9 \cdot 10^{-4}$ T cm^{-1} with a typical average field strength of $B_z = 0.70000$ T, resulting in a value for ω_0 of $187.3 \cdot 10^6$ rad s^{-1}. If we assume a uniform frequency distribution in the range $\omega_0 - \Delta < \omega < \omega_0 + \Delta$, the averaged magnetic moment in the x-direction will be proportional to $\frac{1}{t}\left(\sin(\omega_0 + \Delta) - \sin(\omega_0 - \Delta)\right)$.

the magnetization of the system has dropped to almost zero as a result of the spin axes all pointing in different directions and the macroscopic evidence for the original order the system was prepared in, the free induction decay signal, has faded away.

From a coarse-grained perspective the occurrence of the echo is completely miraculous. When we study the spin-echo experiments in terms of coarse-grained entropy, we will be led to the conclusion that the nuclear spin system spontaneously evolves from a high (coarse-grained) entropy state to a low (coarse-grained) entropy state. Using coarse graining we will be led to the misleading (indeed false) observation that the system has reached a near-equilibrium state at time $t = \tau$ and that it subsequently evolves away from equilibrium upon the application of the second rf pulse. One would therefore conclude that the spin-echo experiments constitute a counterexample to the Second Law of Thermodynamics. This is a wrong conclusion of course; the experiments do not actually contradict the Second Law. The spin-echo experiments are an example of a physical system for which the dynamical evolution can be reversed at the microscopic scale and in this sense the process by which this reversal is accomplished might be called a 'Loschmidt demon'. However, in the spin-echo experiments we do not have a situation where a system evolves spontaneously from a high entropy state to a low entropy state.

As Mayer and Mayer[(15)] point out, this is obvious given the fact that in order to measure the entropy of the spin system, one has to remove the system from the magnetic apparatus which produces the various magnetic pulses in order to be able to determine the entropy difference between the system and some standard state of known entropy by measuring the heat flow into or out of the system. This must be done using a *reversible* path. However, consider the following sequence of operations on the spin system: 1) remove the spin system from the magnetic apparatus just before $t = \tau$ in order to measure the entropy by measuring the heat flow, 2) restore the entropy state of the system by reversing the heat path, 3) place the spin system back in the magnetic field and 4) apply the second rf pulse. We then find that although we do measure a high entropy state for the system, the system has lost the ability to produce the echo signal upon application of the second rf pulse. In other words; the measurement of the entropy of the system was *not* by a reversible path. The measurement destroys the correlations in the system and thus prevents a return to the initial state. When the heat path is reversed, only the average value of the angle between the spin axes and the x axis is reproduced; the individual spins 'have lost the memory' of their exact angles with the x axes. Therefore, we are not entitled to say that in a spin-echo experiment the spin system is in a high entropy state just before $t = \tau$ and then evolves to a low entropy state, because the only method we have of measuring the entropy of the system actually alters the state of the system. A reversible way of measuring the entropy of the system would consist of leaving the system in the magnetic field until the moment when the echo appears. The heat path in this case is reversible, because when the system is replaced in the magnetic field after reversing the path, its "normal" evolution will continue.

We can now draw the following conclusions. An explanation of non-equilibrium behaviour of thermodynamic systems in terms of Gibbsean ensembles should provide an account of how a system can evolve from an equilibrium

state for one set of macroscopic parameters into an equilibrium set for a new set of macroscopic parameters, in the process increasing its entropy. Such an explanation is complicated by Liouville's theorem, which prevents a uniform distribution on one part of the phase space evolving to a uniform distribution on a larger part of phase space.

In its desire to overcome the constraints placed upon the evolution of the density distribution on phase space by Liouville's theorem, the coarse graining approach introduces a coarse-grained density distribution and studies the evolution of the system in terms of the corresponding coarse-grained entropy. This procedure amounts to ignoring the correlations which are built up in the system under the dynamical evolution. This is illustrated by the study of our model of spin-echo systems. The apparent anti-thermodynamical behaviour of the spin system according to the coarse graining approach arises precisely because this approach ignores the fact that the original order of the system is spread out into correlational information, transforming the order into a kind of "hidden order".

In other words: the problem with invoking coarse graining to account for macroscopic irreversibility arises because it leads to a failure to draw the all important distinction between what Blatt called "quasi-equilibrium" states and true equilibrium states[14] (p. 749). That is, a state which from the macroscopic point of view appears to be an equilibrium state, but which contains all the information about the initial state of the system, is mistaken for a state in which this information is no longer available. In order to obtain a true equilibrium state we need a mechanism which accounts for the actual disappearance of these correlations.

In the case of the spin-echo experiments this mechanism is provided by the relaxation of the spin energy into other forms of energy within the nuclear spin system. The gradual loss of correlational information is made manifest by the gradually diminishing strengths of the echo signals when the rf pulses are applied repeatedly. In other words, it is the interaction of the spin system with its environment which enables the system to achieve a true equilibrium state. If the exchange between spin energy and other forms of energy within the system could be prevented, the system would never be found in a true equilibrium state. This is an example of the approach to non-equilibrium statistical mechanics called interventionism. Here the underlying idea is that no physical system can be completely isolated from its environment and that it is the interaction of the system with this environment which provides the required mechanism for the destruction of correlational information. We will return to the interventionist approach in section 5.

In fact, without destruction of correlations Loschmidt's objection against Boltzmann's H-theorem would hold. Recall that Boltzmann claimed his H-theorem to provide us with an account of irreversibility, on the basis of the fact that it proved the existence of a unique equilibrium state which will be steadily and monotonically approached from any non-equilibrium state.

The way Loschmidt's paradox is set up is by arguing that reversing all the velocities of the particles of an isolated system would result in the system retracing its motion back to its original state, since the microdynamical laws of motion are time-reversal invariant. In other words; for any evolution of a system towards equilibrium there is another possible motion which would take the system away from equilibrium. This symmetry is in contradiction with the irreversibility of Boltzmann's H-theorem.

Boltzmann replied to Loschmidt on the grounds that Loschmidt's arguments didn't do justice to the statistics of systems containing a large number of particles. Let us once again consider a gas which is originally contained in one half of a box and which is then allowed to expand into the other part of the box. The Loschmidt paradox is based on the assumption that if a macroscopic process $I \rightarrow F$ occurs, the reverse process $F \rightarrow I$ would be equally probable, where I is the initial macroscopic state of the system and F is the final macroscopic state. Boltzmann replied to the paradox by arguing that this assumption is not valid. If we list the microstates available to the system in its initial macroscopic state I as $\{I_k\}$ and the microstates available to the system in its final macroscopic state F as $\{F_l\}$ and if we furthermore denote the microstates which are identical to I and F in all respects apart from the fact that all particle velocities have been reversed by $\{\bar{I}_k\}$ and $\{\bar{F}_l\}$ respectively, then according to Boltzmann it is obvious that for a system consisting of a large number of particles almost all microstates I_k will make the system evolve into F, whereas only a small number of the reversed microstates $\bar{F}_l$ will make the system evolve into $\bar{I}$, namely only these microstates which possess the necessary correlations between its particles. In other words, for the case of a gas in a box, only a very small fraction of the set of microstates of the gas which are compatible with the new thermodynamic constraints of the system will be suitable for contraction into the original smaller volume upon velocity reversal of the microstates.

Returning to the spin-echo experiments, we see that this argument breaks down, because as long as no exchange between spin energy and other degrees of freedom in the spin system takes place, the number of microstates I_k is exactly matched by the number of velocity inverted microstates $\bar{F}_l$.

This will in general be true for every situation where the original information about the ordered initial state of a system is preserved and gradually transformed into correlational information, without the correlations being destroyed by some mechanism. This is exactly what Liouville's theorem tells us. To obtain a satisfactory account of non-equilibrium behaviour we need to explain how an ensemble occupying a given volume in phase space consistent with one set of macroscopic parameters can come to occupy a larger volume in phase space once the macroscopic parameters are changed, in spite of Liouville's theorem. Every such account of will have to rely crucially on the introduction of a mechanism for the destruction of correlations.[9]

Using a coarse-grained description amounts to simply ignoring the dynam-

[9]It is worth noticing in passing that Prigogine and co-workers[16] choose a different strategy to deal with the spin-echo experiments without being forced to say that these experiments exhibit anti-thermodynamic behaviour. They introduce a distinction between "normal correlations", which are produced by collisions between particles, and "anomalous correlations", which are introduced by velocity inversions. They then introduce a new definition for entropy, which is supposed to be able to keep track of the existence and subsequent decay of these anomalous correlations. The result would be that in the second half of a spin-echo experiment this entropy would increase, rather than decrease like the coarse-grained entropy or remain constant like the fine-grained entropy, as a result of the decay of anomalous correlations. However, to us this approach seems a non-starter, since the "decay of anomalous correlations" is simply the retracing by the ensemble distribution of its dynamical history. It has nothing to do with an increase of the volume of phase space occupied by the ensemble distribution, which is what one needs for the Gibbs entropy to increase. To show the increase of a newly defined quantity like Prigogine's entropy is irrelevant for the project of explaining thermodynamic behaviour, unless the relation between this entropy and the thermodynamic entropy is established, as is the case for the Gibbs entropy.

ically generated correlational information. Although this may lead to correct predictions in cases where the correlations are actually destroyed, this practice cannot claim to provide an adequate *explanation* of irreversibility. In other words; the *origin* of irreversibility cannot lie in coarse graining methods.[10] It is precisely the fact that for ordinary thermodynamic systems we can produce correct predictions by averaging over microscopic variables that needs to be explained. We thus see that claims like the following one by Denbigh and Denbigh[(13)] (p. 57) are using a misleading meaning of "irreversibility":

> ... it would be counter-intuitive to suppose that the macroscopic aspects of irreversible processes could not occur *without* the external perturbations. To take an example, a gas would surely expand into a vacuum even if the whole system were *perfectly* isolated. [...] Even though complete isolation may be impossible to attain, it would seem wrong to suppose that macroscopic irreversibility would not occur if it were attained.

Surely a gas would expand into the vacuum as a result of the motions of the molecules—a molecule which would have been reflected by the wall of a container proceeds unhindered into the vacuum after the wall has been removed but without a mechanism for the destruction of correlations the probability distribution would not turn into a uniform distribution over the phase space. The analysis of the spin-echo phenomena in the previous sections shows that the latter notion is the correct notion of irreversibility in this context: the irreversible processes described by thermodynamics are not simply changes from a state with a macroscopically discernible order into a state for which this order is merely macroscopically indiscernible, but changes to a state where the correlational information about the initial macroscopic order has vanished on the microscopic level.

Sklar[(17)] (p. 253) also focusses on the loss of macroscopic order as the crucial aspect of irreversible processes:

[10]There is some confusion in the literature about the precise role of the loss of correlations with respect to irreversibility. Denbigh and Denbigh[(13)] (p. 142) in discussing the spin-echo experiments write:

> Although some small entropy reduction might be attributed to the partial reversal which is to be seen at the macrolevel, this is much more than compensated for by a major effect which is the continuous entropy production occuring at the microlevel due to the progressive loss of correlations.

It is difficult to understand what Denbigh and Denbigh mean with this statement. When they talk about an entropy reduction and an entropy production, either they must be considering in both cases the fine-grained entropy, or they are considering the coarse-grained entropy with respect to the entropy decrease and the fine-grained entropy with respect to the increase of entropy.

In the first case the observation that a decrease in entropy might be attributed to the system is wrong; as long as we don't take the destruction of correlational information into account, the fine-grained entropy remains constant, in agreement with Liouville's theorem.

In the second case the statement is inconsistent. One cannot compare quantities of entropy for two different types of entropy and then conclude that the difference between the increase of fine-grained entropy and the decrease of coarse-grained entropy is greater than zero. It does not make sense to use on the one hand a definition of entropy involving a simple notion of order (where a situation with all the spin axes pointing in the same direction is defined to be of a higher entropy than any situation where this is not the case) and then to compare the reduction of the entropy thus defined with the increase in fine-grained entropy, which is connected to the number of microstates compatible with the specified macroscopic parameters for the system.

> ...in the first stages of the spin-echo process there is an 'entropy increase' of the familiar sort. That is, there is a dissipation of macroscopic order (the internal magnetization due to the alignment of the spins) into macroscopic disorder or uniformity (with the spins uniformly distributed in all directions in the plane into which they were originally flipped). Doesn't the spin-echo experiment really show us that at least in one case, there is the macroscopic behavior of the kind we normally take ourselves to be explaining in thermodynamics, despite the *provable absence* of outside intervention? This absence is revealed in the reconstructibility of the original order by the second flip. This kind of entropy increase is, plainly, merely 'coarse-grained' increase. But doesn't the experiment convince us that even when fine grained entropy is conserved, we should still expect an asymmetric increase of the kind of entropy familiar to us from thermodynamics? To be sure, the information about the original order of the system in question can't vanish from the system as a whole without something like outside intervention to allow it to dissipate into the outside environment. But what the spin echo experiment shows us is that there is loss of information to be accounted for even when the full information has spread itself out into correlations among the micro-components of the system without truly disappearing altogether.

We disagree with Sklar: the first stages of the spin-echo experiments do *not* show the behaviour we normally take ourselves to be explaining; it is true equilibration, not apparent equilibration which is typical of thermodynamic behaviour. This is illustrated by the case of an imaginary coarse-grainer. Such a person will predict the wrong results. Suppose she just walks by and happens to see the system at the moment the free induction decay signal has died out and the second rf pulse has been applied. She will then predict that the system will remain in the apparently disordered state; but in fact, of course, the system will return to a state with all the spin axes aligned along the same axis so that the echo signal is emitted. The echo will come as a complete surprise to the coarse-grainer. For the interventionist the echo is no surprise at all of course since he knows that the system has been prepared in a very special way (that minimises the effect of interventionist perturbations). The kind of thermodynamic behaviour we would like to explain using statistical mechanics is the behaviour which leads to the usual situation in which an innocent observer unaware of the history of the system will actually make the *right* prediction, namely that the system is going to stay in the equilibrium state for all future times. It is these states which can truly be called equilibrium states. The fact that in practice for almost all thermodynamic systems we cannot achieve the analogue of a Loschmidt-type reversal should not mislead us into thinking that there is an *a priori* difference between spin-echo systems and all other systems. On the contrary, what the spin-echo experiments show is that typical thermodynamic behaviour needs to be accounted for in terms of the approach to true equilibrium states, not the approach to quasi-equilibrium states.

5 Interventionism

In the previous sections we saw that according to the coarse graining approach, it is the accidental shortcomings of the observer which gives rise to the emergence of irreversibility. The fact that no observer can make measurements with unlimited resolution is given as the justification to introduce a direct coarse graining on the phase space of the system, the scale of which represents the measurer's resolution. The summing over degrees of freedom in each coarse-grained cell then gives rise to the required suppression of statistical correlations, allowing a non-equilibrium density distribution to evolve to an equilibrium distribution.

The analysis of the spin-echo experiments shows that this approach fails to acknowledge the distinction between quasi-equilibrium states and true equilibrium states. In situations where the equilibrium distribution actually evolves to a true equilibrium state, a coarse-grained description will lead to the correct predictions, but this leaves open the question as to the origin of this behaviour—that is, the fact that the averaging over degrees of freedom gives the right predictions does not in itself explain what the origin of the suppression of statistical correlations is.

What is needed for the approach to equilibrium is for a system to lose its coherence. Since an isolated system will retain its coherence, the only way to account for non-equilibrium behaviour is to focus on the fact that no physical system can be completely isolated from its environment. The origin of irreversibility is then seen to lie in the interaction between a system and its environment. On this so-called interventionist account, statistical correlations are dissipated into the larger system consisting of the environment. This means that for observations which are restricted to the system proper, the correlational information becomes unavailable, although there is no destruction of correlations. In other words, it is the fact that thermodynamic systems are limited, non-isolated systems which gives rise to the emergence of irreversible behaviour.

Thus we see that on this account irreversibility emerges as a result of physical properties of thermodynamic systems, namely that they are coupled to other degrees of freedom pertaining to their environment. This account has to be sharply distinguished from the coarse graining account of irreversibility, which relies on contingent facts about our limitations with respect to the accuracy with which we can perform measurements on the system.

It is interesting to notice that the interventionist approach may be expected to produce much more realistic relaxation times than the approaches based on mixing properties of the dynamics governing the time evolution of the ensemble distribution. Recall from Section 3 that only in the limit of time going to infinity true equilibrium would be obtained by our model system, which dynamics satisfies the mixing condition. Blatt[(14)] (p. 755), discussing a system of ideal gas particles interacting with the wall of the container, shows that the time scale on which complete loss of coherence in the system of gas particles will be obtained as a result of this interaction with the wall is of order $t \sim 1$ sec.

Of course one could appeal to stronger ergodic properties than mixing to reproduce the finite relaxation times found in thermodynamic systems. However, in general we reject these ergodic approaches, since they do not appear to be relevant for realistic systems, as a result of, for example, the KAM-theorem.[11]

[11] See Sklar[(17)] for a detailed discussion of the problems surrounding the approaches based

We now turn to a detailed discussion of a model for the interventionist approach to non-equilibrium statistical mechanics. One of the earliest accounts of interventionism is given by Bergmann and Lebowitz[(18)]. They consider a system interacting with a reservoir consisting of an infinite number of similar parts which are disconnected (i.e. the influence the components of the reservoir exert on each other is taken to be negligible). Prior to interaction statistical independence is assumed between each part of the reservoir and the system. Of course, once the system starts interacting with any part of the environment, this statistical independence will be lost. Furthermore, the interaction is assumed to be of an impulsive nature; each part of the reservoir interacts with the system for a brief span of time only, resulting in the representative point in system phase space being moved a finite distance that depends both on its original location and on the state of the reservoir just prior to the interaction. Finally it is assumed that each of the parts of the reservoir interacts only once with the system.

A transition probability density $K(x', x)$ is determined by averaging over the possible states of the reservoir, giving the probability $K(x', x)dx'dt$ that the representative point of the system known to be at the location x in system phase space will be thrown into the volume element dx' within the time interval dt. The Liouville equation for the probability density ρ in system phase space is then given by:

$$\frac{\partial\rho(x,t)}{\partial t} + (\rho, H)_x = \int_{x'} \left[K(x,x')\rho(x') - K(x',x)\rho(x)\right] dx' \tag{14}$$

As a result of the fact that the Liouville equation is now modified by the term describing the effect of the interaction of the system with the environment, this equation no longer implies that the system's (fine-grained) entropy has to remain constant.

Bergmann and Lebowitz show that, given certain conditions which amount to the assumption that the cross sections for a transition and the time-reversed transition are equal[12], the system governed by equation (14) will monotonically approach the canonical distribution.

We now turn to the question of temporal asymmetry. Starting with an ensemble representing a system in a non-equilibrium (low entropy) state, the

on the ergodic hierarchy.

[12]The value of $K(x', x)$, i.e. the probability that a transition from the state x to the state x' will occur given that the system initially is in the state x, depends on the distribution of the reservoir in the reservoir phase space, as well as on the intrinsic probability (or cross section) for a collision to happen if both system and reservoir are in suitable states for a collision. As far as the distribution of the reservoir is concerned, the assumption is that the parts of the reservoir are in a canonical distribution. The assumptions with regard to the cross section are of a more subtle nature. As a result of the time reversal invariance of the microdynamical laws of motion, the cross sections for a transition from x to x' and for what is termed the "properly reversed" transition $\bar{x}'$ to $\bar{x}$, are equal. (Here the transformation $x \to \bar{x}$ denotes the time-reversal transformation under which the Hamiltonian remains the same function of its arguments. In classical mechanics this transformation involves a change in the sign of the time coordinate and of all momentum coordinates. In quantum mechanics it involves changing the sign of the time coordinate and replacing the wave function by its complex conjugate.) However, Bergmann and Lebowitz need a stronger condition than this in order to prove the monotonic approach to equilibrium. They have to assume that the cross sections for the transition from x to x' and what they call the "directly reversed" transition x' to x are also equal.

interventionist model given above shows how the system will evolve towards an equilibrium state as a result of the interactions with the environment. In other words, the monotonic approach of a system to the state of maximum entropy can now be achieved since the ordinary constraint on the entropy arising from Liouville's equation is lifted as a result of the additional term describing the interaction of the system with the environment. However, since the microdynamical laws of motion are time-reversal invariant, every purely dynamical argument will necessarily provide time-symmetric results. The question we now have to address is therefore: would not the interventionist model come up with exactly the same results when applied in the reverse time direction? That is, if at a certain time we consider an ensemble of systems all of which are in a non-equilibrium state and which have interacted with an environment in their past, are not we forced to conclude that as a result of the random perturbations from the environment the ensemble distribution will approach the equilibrium distribution *into the past time direction*? Obviously, this would land the interventionist approach into trouble, since this time-reversed conclusion does not correspond with our empirical evidence.

Sklar[17] (p. 254) argues that the only possible way to prevent the interven tionist line of arguing from being applied into the past time direction would be to argue that the intervention from the environment is itself time-directed.

> Because intervention is causation, and because causation is from past to future, the intervention can only modify the ensemble toward the future direction of time. But without some deeper understanding of what is being used here, some understanding of how causation is playing some role over and above lawlike correlations of states, this sounds more like an a priori restrictive instruction on when to use statistical mechanics and when not to. This is like O. Penrose's "principle of causality"[19] (p. 1941) concerning ensembles, which says that "the phase space density at any time is completely determined by what happened to the system before that time and is unaffected by what will happen to the system in the future." But is it an explanatory account of why the asymmetry holds in the world?

The answer to the latter question is: no, this is not a satisfactory *explanation* of the observed asymmetry in the world. It is at best a *description* of what the asymmetry consist in.

However, in the Bergmann-Lebowitz model it is not necessary to invoke causality in order to explain the observed asymmetry in the world. In this model time-asymmetry arises as a result of 1) the system-environment cut, 2) the structure of the environment (non-interacting parts), 3) the assumption that each part of the environment interacts only once with the system and 4) the assumption that at $t=0$ the system and the environment are statistically independent. Notice that assumptions 2) and 3) might not be straightforwardly justifiable for real physical systems, such as the spin systems used in the spin-echo experiments. When we take the environment of the nuclear spin system to be the other degrees of freedom of the spin system, such that the interaction between system and environment gives rise to the relaxation of the spin energy into other forms of energy, it is not obvious why the system would exchange energy with each degree of freedom only once and why energy would not be exchanged between the other degrees of freedom. This problem can be solved

once we realize that each part of the environment of the system will itself have an environment with which it will interact. In this way the correlational information, which initially is fully contained in the system, will gradually dissipate into an ever growing environment. In other words, the parts of the immediate environment of the system will continuously be able to present themselves to the system as if they were a part the system had not interacted with before.

The net result of these assumptions for the system amounts to the analogue of Boltzmann's Stoßzahlansatz. However, Boltzmann simply had to assume that the Stoßzahlansatz holds at each moment of the dynamical evolution of the system, an assumption which is provably false. On the interventionist account of irreversibility it is the fact that whereas obervations are restricted to the system proper, this system is in interaction with an environment with a large number of degrees of freedom which are not observed. This allows us to model the interaction with the environment by a stochastic term, giving rise to the modified Liouville equation (14).

As we saw above, the value of the transition probability $K(x', x)$ is independent of the ensemble distribution in system phase space. In other words, the correlations which are created between the system and a particular part of the reservoir as a result of their interaction, are irrelevant for the later evolution of the system, because that part of the reservoir will not interact with the system anymore and the transition probability density in the system phase space does not depend on the effects of the earlier interaction with the part of the reservoir in question. However, although the value of $K(x', x)$ is independent of the distribution in system phase space, it does depend on the distribution of the reservoir. That is, the influence the system exerts at one part of the reservoir will depend on the influence it exerted earlier on other parts of the reservoir. This is why the argument cannot be applied in the reversed time direction to argue that equilibrium will be approached into the past; in the ordinary time direction the "incoming" influences are the influences from the environment on the system and these are uncorrelated, but in the reversed time direction the "incoming" influences are the influences the systems exerts on its environment and these will be correlated.

Effectively the system is "exporting" its correlations to the environment, but, of course, the argument can be repeated for the larger system consisting of the original system under investigation and its immediate environment, which will exhibit an increase in fine-grained entropy, due to perturbations from the "environment of the environment".

But, finally the question arises what the implications of the interventionist approach are for the universe as a whole. Since the universe itself does not have an environment to interact with, it follows that its entropy must be constant in time. Is not this in contradiction with what cosmologists standardly describe as the cosmic entropy increase? We think not. The definitions of entropy used in cosmological discussions are coarse-grained ones, based on notions of order and disorder in the matter distribution in the universe (see for example Penrose(20) and Hawking(21)). The fact that entropy so defined can increase is not in contradiction with a fine-grained entropy which remains constant for the universe as a whole.

Appendix

A The change of the density distribution under the dynamical law

We assume $t > \frac{\delta}{\omega_m}$, $\delta \ll 2\pi$. We have to distinguish between the following three cases; $\frac{\delta}{\omega_m} < t < \frac{2\pi-\delta}{\omega_m}$, $\frac{n\cdot 2\pi-\delta}{\omega_m} \leq t < \frac{n\cdot 2\pi}{\omega_m}$ and $\frac{n\cdot 2\pi}{\omega_m} \leq t < \frac{(n+1)2\pi-\delta}{\omega_m}$, with $n = \mathrm{int}\left(\frac{\omega_m t}{2\pi}\right) + 1$.

For the case $\frac{\delta}{\omega_m} < t < \frac{2\pi-\delta}{\omega_m}$ we have:

<u>$0 \leq x < \delta$:</u>

$$\begin{aligned} \rho(t) &= \rho_0\,, \quad 0 \leq \omega \leq \tfrac{x}{t} \\ &= 0, \qquad \omega > \tfrac{x}{t} \end{aligned} \tag{15}$$

<u>$\delta \leq x < \omega_m t$:</u>

$$\begin{aligned} \rho(t) &= 0, \qquad 0 \leq \omega < \tfrac{x-\delta}{t} \\ &= \rho_0\,, \quad \tfrac{x-\delta}{t} \leq \omega \leq \tfrac{x}{t} \\ &= 0, \qquad \tfrac{x}{t} < \omega \leq \omega_m \end{aligned} \tag{16}$$

<u>$\omega_m t \leq x < \omega_m t + \delta$:</u>

$$\begin{aligned} \rho(t) &= 0, \qquad 0 \leq \omega < \tfrac{x-\delta}{t} \\ &= \rho_0\,, \quad \tfrac{x-\delta}{t} < \omega < \omega_m \end{aligned} \tag{17}$$

<u>$\omega_m t + \delta \leq x < 2\pi$:</u>

$$\rho(t) = 0, \quad 0 \leq \omega \leq \omega_m. \tag{18}$$

For the case $\frac{n\cdot 2\pi-\delta}{\omega_m} \leq t < \frac{n\cdot 2\pi}{\omega_m}$ we have:

<u>$0 \leq x < \omega_m t + \delta - n\cdot 2\pi$:</u>

$$\begin{aligned} \rho(t) &= \rho_0\,, \quad 0 \leq \omega \leq \tfrac{x}{t} \\ &\qquad\quad \tfrac{x-\delta+i2\pi}{t} \leq \omega \leq \tfrac{x+i2\pi}{t}, \; i=1,\ldots,(n-1) \\ &\qquad\quad \tfrac{x+n2\pi-\delta}{t} < \omega < \omega_m \\ &= 0\,, \quad \tfrac{x+i2\pi}{t} < \omega < \tfrac{x-\delta+(i+1)2\pi}{t}, \; i=0,\ldots,(n-1) \end{aligned} \tag{19}$$

<u>$\omega_m t + \delta - n\cdot 2\pi \leq x < \delta$:</u>

$$\begin{aligned} \rho(t) &= \rho_0\,, \quad 0 \leq \omega \leq \tfrac{x}{t} \\ &\qquad\quad \tfrac{x-\delta+i2\pi}{t} \leq \omega \leq \tfrac{x+i2\pi}{t}, \; i=1,\ldots,(n-1) \\ &= 0\,, \quad \tfrac{x+i2\pi}{t} < \omega < \tfrac{x-\delta+(i+1)2\pi}{t}, \; i=0,\ldots,(n-2) \\ &\qquad\quad \tfrac{x+(n-1)2\pi}{t} < \omega < \omega_m \end{aligned} \tag{20}$$

$\underline{\delta \leq x < \omega_m t - (n-1)2\pi}$:

$$
\begin{aligned}
\rho(t) \; &= \rho_0\,, \quad \tfrac{x-\delta+i2\pi}{t} \leq \omega \leq \tfrac{x+i2\pi}{t},\; i=0,\ldots,(n-1) \\
&= 0\,, \quad 0 \leq \omega < \tfrac{x-\delta}{t} \\
&\qquad\;\; \tfrac{x+i2\pi}{t} < \omega < \tfrac{x-\delta+(i+1)2\pi}{t},\; i=0,\ldots,(n-2) \\
&\qquad\;\; \tfrac{x+(n-1)2\pi}{t} < \omega \leq \omega_m
\end{aligned}
\tag{21}
$$

$\underline{\omega_m t - (n-1)2\pi \leq x < 2\pi}$:

$$
\begin{aligned}
\rho(t) \; &= \rho_0\,, \quad \tfrac{x-\delta+i2\pi}{t} \leq \omega \leq \tfrac{x+i2\pi}{t},\; i=0,\ldots,(n-2) \\
&\qquad\;\; \tfrac{x-\delta+(n-1)2\pi}{t} \leq \omega \leq \omega_m \\
&= 0\,, \quad 0 \leq \omega < \tfrac{x-\delta}{t} \\
&\qquad\;\; \tfrac{x+i2\pi}{t} < \omega < \tfrac{x-\delta+(i+1)2\pi}{t},\; i=0,1,\ldots,(n-2)
\end{aligned}
\tag{22}
$$

For the case $\frac{n\cdot 2\pi}{\omega_m} \leq t < \frac{(n+1)2\pi-\delta}{\omega_m}$ we have:

$\underline{0 \leq x < \delta}$:

$$
\begin{aligned}
\rho(t) \; &= \rho_0\,, \quad 0 \leq \omega \leq \tfrac{x}{t} \\
&\qquad\;\; \tfrac{x-\delta+i2\pi}{t} \leq \omega \leq \tfrac{x+i2\pi}{t},\; i=1,\ldots,n \\
&= 0\,, \quad \tfrac{x+i2\pi}{t} < \omega \leq \tfrac{x-\delta+(i+1)2\pi}{t},\; i=0,\ldots,(n-1) \\
&\qquad\;\; \tfrac{x+n\cdot 2\pi}{t} < \omega \leq \omega_m
\end{aligned}
\tag{23}
$$

$\underline{\delta \leq x < \omega_m t - n\cdot 2\pi}$:

$$
\begin{aligned}
\rho(t) \; &= \rho_0\,, \quad \tfrac{x-\delta+i2\pi}{t} \leq \omega \leq \tfrac{x+i2\pi}{t},\; i=0,\ldots,n \\
&= 0\,, \quad 0 \leq \omega < \tfrac{x-\delta}{t} \\
&\qquad\;\; \tfrac{x+(i-1)2\pi}{t} < \omega < \tfrac{x-\delta+i2\pi}{t},\; i=1,\ldots,n \\
&\qquad\;\; \tfrac{x+n\cdot 2\pi}{t} < \omega < \omega_m
\end{aligned}
\tag{24}
$$

$\underline{\omega_m t - n\cdot 2\pi \leq x < \omega_m t + \delta - n\cdot 2\pi}$:

$$
\begin{aligned}
\rho(t) \; &= \rho_0\,, \quad \tfrac{x-\delta+i2\pi}{t} \leq \omega \leq \tfrac{x+i2\pi}{t},\; i=0,\ldots,(n-1) \\
&\qquad\;\; \tfrac{x-\delta+(n-1)2\pi}{t} \leq \omega \leq \omega_m \\
&= 0\,, \quad 0 \leq \omega < \tfrac{x-\delta}{t} \\
&\qquad\;\; \tfrac{x+(i-1)2\pi}{t} < \omega < \tfrac{x-\delta+i2\pi}{t},\; i=1,\ldots,n
\end{aligned}
\tag{25}
$$

$\underline{\omega_m t + \delta - n \cdot 2\pi \leq x < 2\pi}$:

$$\begin{aligned} \rho(t) \quad &= \rho_0\,, \quad \tfrac{x+i2\pi-\delta}{t} < \omega \leq \tfrac{x+i2\pi}{t},\ i{=}0,\ldots,(n-1) \\ &= 0\,, \quad 0 \leq \omega \leq \tfrac{x-\delta}{t} \\ &\qquad\quad \tfrac{x+(i-1)2\pi}{t} < \omega < \tfrac{x-\delta+i2\pi}{t},\ i{=}1,\ldots,(n-1) \\ &\qquad\quad \tfrac{x+(n-1)2\pi}{t} < \omega \leq \omega_m \end{aligned} \tag{26}$$

B The area of a coarse-graining box occupied by striations

In order to find the area A of any coarse-graining box of size $\Delta x \Delta \omega$ occupied by striations we introduce the notions of "standard striations" and "edge striations" (see Fig. 5). A standard striation is defined as a complete striation, in the sense that it occupies an area $\frac{\delta}{t} \cdot \Delta x$. We denote the number of standard striations in a box by N_{st}. An edge striation is defined as any striation which is truncated by the top or bottom edges of the box. The number of edge striations in a box is denoted by N_{ed}.

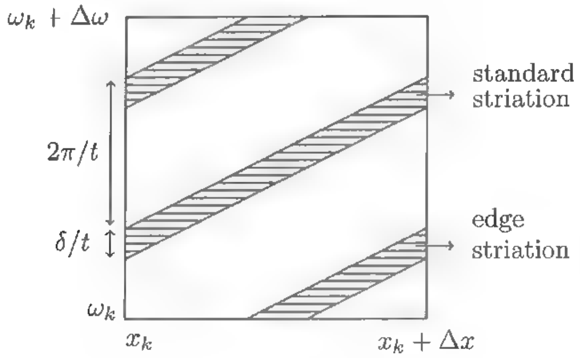

Figure 5: Edge striations and standard striations in a coarse graining box.

For the area A of the box occupied by striations we now have:

$$N_{st} \cdot \frac{\delta}{t} \cdot \Delta x \leq A < (N_{st} + N_{ed}) \cdot \frac{\delta}{t} \cdot \Delta x \tag{27}$$

We now proceed with computing upper and lower bounds on N_{st} and N_{ed}. The following lemma gives us an upper bound on N_{ed}:

Lemma 1

$$N_{ed} \leq 2 \tag{28}$$

Proof Consider a bottom edge striation in its 'highest' position (see Fig. 6). The next striation below it is shifted down by $\frac{2\pi}{t}$, with its top side $\frac{2\pi-\delta}{t}$ below the lower side of the edge striation. The condition for this to be another edge striation of the box in question is

$$\frac{2\pi - \delta}{t} < \frac{\Delta x}{t} \tag{29}$$

But Δx is chosen so that $\Delta x \ll (2\pi - \delta)$, so the condition for a second edge striation cannot be fulfilled. Applying the same argument to the top edge of

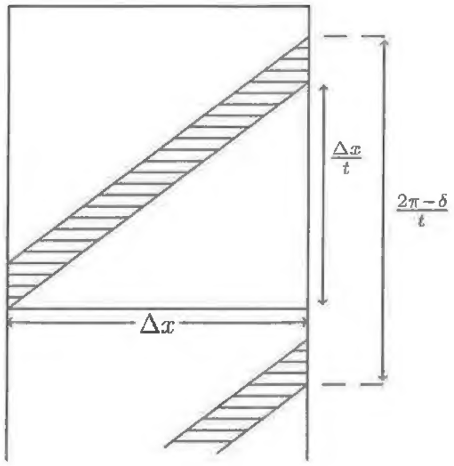

Figure 6: Edge striation in a coarse graining box.

the box, the lemma follows.

We now have the following upper and lower bounds for the area A:

$$N_{st} \cdot \frac{\delta}{t} \cdot \Delta x \leq A < (N_{st} + 2) \cdot \frac{\delta}{t} \cdot \Delta x \tag{30}$$

It remains to estimate N_{st}. We denote the l.u.b. on N_{st} by N^u_{st} and the g.l.b. on N_{st} by N^l_{st}. We have the following lemma:

Lemma 2

$$N^u_{st} = N^l_{st} + 1 \tag{31}$$

Proof

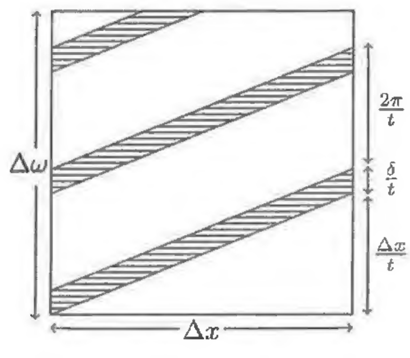

Figure 7: Upper and lower bounds for N_{st}.

Referring to Fig. 7 the upper bound obtains when the first standard striation is in its 'lowest' position. Hence

$$N^u_{st} = \text{int}\left(\frac{\Delta\omega - \delta/t - \Delta x/t}{2\pi/t}\right) \tag{32}$$

Similarly, again referring to Fig. 7 the lower bound obtains when the second standard striation is in its 'lowest' position. So,

$$\begin{aligned} N_{st}^{l} &= \mathrm{int}\left(\frac{\Delta\omega - \delta/t - \Delta x/t - 2\pi/t}{2\pi/t}\right) \\ &= N_{st}^{u} - 1 \end{aligned} \tag{33}$$

Q.E.D.

From (32) and (33) it follows that:

$$\left(\frac{\Delta\omega - \delta/t - \Delta x/t}{2\pi/t}\right) - 2 < N_{st} \leq \left(\frac{\Delta\omega - \delta/t - \Delta x/t}{2\pi/t}\right) \tag{34}$$

Combining this with equation (30), we get:

$$\left(\frac{\Delta\omega \cdot t - \delta - \Delta x}{2\pi} - 2\right) \cdot \frac{\delta \cdot \Delta x}{t} < A < \left(\frac{\Delta\omega \cdot t - \delta - \Delta x}{2\pi} + 2\right) \cdot \frac{\delta \cdot \Delta x}{t} \tag{35}$$

Now let $t \to \infty$. Then in the limit we have $A \to \frac{\delta}{2\pi} \cdot \Delta x \Delta\omega$, as was demonstrated on the basis of intuitive arguments in section 3.

C Computation of the averaged magnetic moment as a function of time

To compute the averaged magnetic moment in the initial direction of magnetization we have to determine the marginal distribution in x. Whereas the marginal distribution in ω is constant in time and uniform over the interval $(0, \omega_m)$ (it is given by the density function $f(\omega) = \frac{\delta}{\delta\omega_m} = \frac{1}{\omega_m}$), the marginal distribution in x changes over time (see Fig. 8).

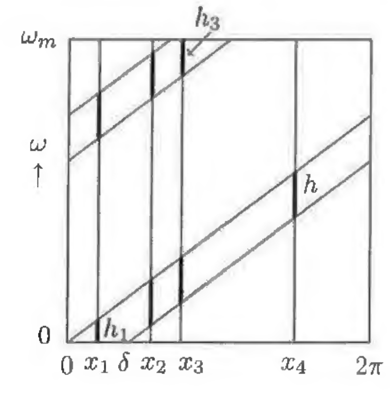

Figure 8: The marginal distribution in x. Here $h = \frac{\delta}{t}$, $h_1 = \frac{x_1}{t}$ and $h_3 = \frac{\omega_m t - 2\pi + \delta - x_3}{t}$ provide illustrative contributions for calculating the marginal distributions.

For sufficiently large t the distribution in x becomes uniform over the interval $(0, 2\pi)$ and is given by the density function

$$f(x) \sim \frac{\omega_m}{2\pi/t} \cdot \frac{\delta}{t} \cdot \frac{1}{\delta\omega_m} = \frac{1}{2\pi}. \tag{36}$$

However, for finite t the distribution is not uniform. Once again we distinguish between three different cases; $\frac{\delta}{\omega_m} < t < \frac{2\pi-\delta}{\omega_m}$, $\frac{n\cdot 2\pi-\delta}{\omega_m} \leq t < \frac{n\cdot 2\pi}{\omega_m}$ and $\frac{n\cdot 2\pi}{\omega_m} \leq t < \frac{(n+1)2\pi-\delta}{\omega_m}$, with $n = \mathrm{int}\left(\frac{\omega_m t}{2\pi}\right) + 1$.

For the case $\frac{\delta}{\omega_m} < t < \frac{2\pi-\delta}{\omega_m}$ we have:

$$
\begin{aligned}
f(x,\, t) \;&= \tfrac{x}{t} \cdot \tfrac{1}{\delta\omega_m}\,, && 0\leq x<\delta \\
&= \tfrac{\delta}{t} \cdot \tfrac{1}{\delta\omega_m}\,, && \delta\leq x<\omega_m t \\
&= \tfrac{\omega_m t+\delta-x}{t} \cdot \tfrac{1}{\delta\omega_m}\,, && \omega_m t\leq x<\omega_m t+\delta \\
&= 0, && \omega_m t+\delta\leq x<2\pi
\end{aligned}
\tag{37}
$$

For the case $\frac{n\cdot 2\pi-\delta}{\omega_m} \leq t < \frac{n\cdot 2\pi}{\omega_m}$ we have:

$$
\begin{aligned}
f(x,\, t) \;&= \tfrac{n\delta+\omega_m t-n\cdot 2\pi}{t} \cdot \tfrac{1}{\delta\omega_m}\,, && 0\leq x<\omega_m t+\delta-n\cdot 2\pi \\
&= \left((n-1)\cdot \tfrac{\delta}{t} + \tfrac{x}{t}\right) \cdot \tfrac{1}{\delta\omega_m}\,, && \omega_m t+\delta-n\cdot 2\pi\leq x<\delta \\
&= n \cdot \tfrac{\delta}{t} \cdot \tfrac{1}{\delta\omega_m}\,, && \delta\leq x<\omega_m t-(n-1)2\pi \\
&= \tfrac{n\delta+\omega_m t-(n-1)\cdot 2\pi-x}{t} \cdot \tfrac{1}{\delta\omega_m}\,, && \omega_m t-(n-1)2\pi\leq x<2\pi
\end{aligned}
\tag{38}
$$

For the case $\frac{n\cdot 2\pi}{\omega_m} \leq t < \frac{(n+1)2\pi-\delta}{\omega_m}$ we have:

$$
\begin{aligned}
f(x,\, t) \;&= \left(\tfrac{x}{t} + n\cdot\tfrac{\delta}{t}\right) \cdot \tfrac{1}{\delta\omega_m}\,, && 0\leq x<\delta \\
&= (n+1) \cdot \tfrac{\delta}{t} \cdot \tfrac{1}{\delta\omega_m}\,, && \delta\leq x<\omega_m t-n\cdot 2\pi \\
&= \tfrac{n\delta+\omega_m t-n\cdot 2\pi-x}{t} \cdot \tfrac{1}{\delta\omega_m}\,, && \omega_m t-n\cdot 2\pi\leq x<\omega_m t+\delta-n\cdot 2\pi \\
&= n \cdot \tfrac{\delta}{t} \cdot \tfrac{1}{\delta\omega_m}\,, && \omega_m t+\delta-n\cdot 2\pi\leq x<2\pi
\end{aligned}
\tag{39}
$$

We can now evaluate the the quantity $M(t) = \int_0^{2\pi} f(x,t)\cos x dx$ by integrating over the appropriate intervals with the appropriate values for the density function $f(x,t)$. Straightforward calculation gives:

$$
M(t) = \frac{1}{\delta\omega_m} \cdot \frac{1}{t}\left(\cos(\omega_m t) - \cos(\omega_m t + \delta) + \cos\delta - 1\right), \quad \forall t > \frac{\delta}{\omega_m} \tag{40}
$$

i.e. $M(t) \sim \frac{\sin(\omega_m t)}{t}$ for $\delta \ll 2\pi$. With $t = \frac{\delta}{\omega_m}$, $\delta \ll 2\pi$, we find

$$
M\left(\frac{\delta}{\omega_m}\right) \sim \frac{1}{\delta^2}(2\cos\delta - \cos 2\delta - 1) \simeq 1 - o(\delta), \tag{41}
$$

as we would expect.

References

[1] J.W. Gibbs, *Elementary Principles in Statistical Mechanics* (Original edition 1902. Dover edition: Dover Publications, New York, 1960).

[2] R.C. Tolman, *The Principles of Statistical Mechanics* (Oxford University Press, Oxford, 1938).

[3] P. Ehrenfest and T. Ehrenfest, *Encykl. Math. Wiss.* **4**, No. 32 (1911). (English translation: *The Conceptual Foundations of the Statistical Approach in Mechanics* (Cornell University Press, Ithaca, 1959)).

[4] I.E. Farquhar, *Ergodic theory in statistical mechanics* (Wiley Interscience, New York, 1964).

[5] P.T. Landsberg, *Thermodynamics and Statistical Mechanics* (Oxford University Press, Oxford, 1978).

[6] O. Penrose, *Foundations of Statistical Mechanics* (Pergamon Press, Oxford, 1970).

[7] J. Bricmont, "Science of Chaos or Chaos in Science?", in *The Flight from Science and Reason*, New York Academy of Science Annals, Vol. 775, p. 131 (1996).

[8] J.L. Lebowitz, *Physics Today* **46**, p. 32. Replies in *Physics Today* **47**, p. 113 (1994)

[9] E.L. Hahn, *Phys. Rev.* **80**, p. 580 (1950).

[10] E.L. Hahn, *Phys. Rev.* **88**, p. 1070 (1952).

[11] W.K. Rhim, A. Pines and J.S. Waugh, *Phys. Rev.* **B3**, p. 684 (1971).

[12] E.L. Hahn, *Physics Today* **6** (Vol. 11), p. 4 (1953).

[13] K.G. Denbigh and J.S. Denbigh, *Entropy in Relation to Incomplete Knowledge* (Cambridge University Press, Cambridge, 1985).

[14] J.M. Blatt, *Prog. Theor. Phys.* **22**, p. 745 (1959).

[15] J.E. Mayer and M.G. Mayer, *Statistical Mechanics* (Wiley, New York, 1977).

[16] I. Prigogine, C. George, F. Henin and L. Rosenfeld, *Chem. Scripta* **4**, p. 5 (1973).

[17] L. Sklar, *Physics and Chance* (Cambridge University Press, Cambridge, 1993).

[18] P.G. Bergmann and J.L. Lebowitz, *Physical Review*, **99**, p. 578 (1955).

[19] O. Penrose, *Rep. Prog. Phys.* **42**, p. 1937 (1979).

[20] R. Penrose, 'Singularities and time-asymmetry' in S.W. Hawking and W. Israel (eds.) *General Relativity. An Einstein Centenary Survey* (Cambridge University Press, Cambridge, 1979).

[21] S.W. Hawking, *Phys. Rev. D* **32**, p. 2489 (1985).